



Comparing the degradation of acetochlor to RhB using BiOBr under visible light: A significantly different rate-catalyst dose relationship

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ARTICLE INFO

Article history:

Received 7 April 2015

Received in revised form 28 June 2015

Accepted 4 August 2015

Available online 10 August 2015

Keywords:

Bismuth oxide bromide

Acetochlor

RhB

Unique adsorption behavior

Photodegradation

ABSTRACT

In this study, a weakly polar pesticide acetochlor in water was tried to degrade by BiOBr catalysts under visible light irradiation. Its degradation reaction rate increased exponentially with increasing catalyst dosage, which was significantly different from conventional photocatalytic patterns established for polar or water-soluble pollutants. Thus, the rate-dosage relationship of BiOBr/acetochlor was compared to that of BiOBr/Rhodamine B (RhB) (a typical strong polar dye pollutant in water) at different BiOBr dosages. The degradation rate of RhB increased with the BiOBr dosage and then plateaued due to more catalyst particles blocking the light into the inner solution, which is a typical behavior for heterogeneous photocatalysis of polar organic compounds in aqueous solution. While acetochlor behaved differently, its degradation rate increased exponentially with the BiOBr dosage, and no plateau was observed even up to 9.0 g/L BiOBr dosage. This special rate-dose relationship for weakly polar acetochlor was correlated with a unique adsorption property of BiOBr to acetochlor in water solution. There was a re-distribution effect that always exclude excessive acetochlor adsorbed on BiOBr surface regardless either substrates or BiOBr overdose. This finally resulted in every BiOBr particle having enough adsorption sites available for dissolved dioxygen to function thereby accelerate the degradation of weakly polar organic compounds in water.

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1. Introduction

Acetochlor, which is a chloroacetanilide herbicide, is used for pre-emergence control of weeds for crops, such as beans and corn, and is one of the most widely used herbicides in the world. The aromatic ring and lack of strongly polar bonds (Fig. 1) prevent its binding to soil, so acetochlor is readily transferred from agricultural fields to water to cause environmental pollution. Natural way of the degradation of acetochlor residues in the land, and water is primarily direct photolysis under UV sunlight. The United States Environmental Protection Agency (USEPA) has classified acetochlor as a B-2 carcinogen [1]. Currently, advanced oxidation processes (AOP) for the degradation of acetochlor in water typically utilize

ozone [2,3], the Fenton reagent [4], γ -ray [5] and UV irradiation [6–8], in which acetochlor reacts stoichiometrically with homogeneous oxidants. These treatments can degrade acetochlor quickly, but it is costly to provide the necessary oxidant, such as O_3 , H_2O_2 or high-energy radiation. Therefore, the development of novel heterogeneous photocatalytic systems that are activated by visible light and use the molecular oxygen in air as an oxidant is crucial. The TiO_2 photocatalytic reaction under UV light has been widely used to degrade many organic pollutants in water [9]. However, due to the polarity of its amide bond influenced by the C–Cl and C–O–C bonds within acetochlor molecule, solid oxide photocatalysts, such as TiO_2 , do not provide sufficient adsorption sites for the efficient degradation of acetochlor.

BiOBr responds to both UV and visible light irradiation [10] and has been used to degrade a wide variety of water-soluble organic contaminants including microcystin-LR [11], methyl orange [12–15], rhodamine B (RhB) [16–18], phenol [16], ibuprofen [19], ciprofloxacin [20], tetrabromobisphenol A [21], benzotriazole [22] and guanine [23]. BiOBr has two separate valence bands (i.e., O 2p and Br 4p), and the conduction band is Bi 6p [9]. The excitation

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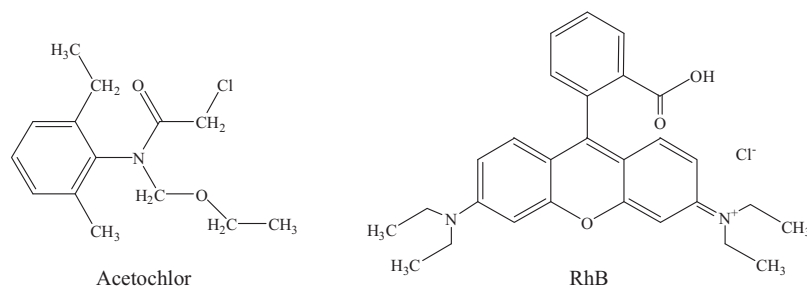


Fig. 1. Structures of acetochlor and RhB.

potential of the two valence bands is 2.6 eV (UV) and 2.25 eV (vis), respectively. The measured band gap of BiOBr is 2.45 eV. Therefore, BiOBr cannot directly oxidize water ($E^0_{\bullet\text{OH}/\text{H}_2\text{O}} = +2.7 \text{ V}$ vs NHE) into hydroxyl radicals ($\bullet\text{OH}$). Instead, the $\bullet\text{OH}$ free radicals are produced by a multi-step reaction on the conduction band, resulting in degradation of refractory organic compounds [24]. BiOBr has tetrahedral symmetry rather than the octahedral symmetry of the commonly used two-component oxide crystals of TiO_2 , CdS and WO_3 . The polarity of the Bi–O bond is also lower than that of the Ti–O bond. These characteristics affect the adsorption and degradation behavior as well as the potential for developing a more effective degradation system for weakly polar organic compounds, such as acetochlor.

In this investigation, the photocatalytic degradation of acetochlor on BiOBr under visible light irradiation ($\lambda > 420 \text{ nm}$) was studied by monitoring total organic carbon (TOC) and chemical oxygen demand (COD) and the concentration of acetochlor using gas chromatography (GC). Our research focused on comparing the degradation of acetochlor with RhB, which is a typical water-soluble pollutant, under identical conditions. The optimal efficiency and relative mechanism for the degradation of the weakly polar acetochlor over BiOBr were determined by quantitatively analyzing the relationship between its degradation rate and catalyst dose. In addition, the dramatic difference in the adsorption vs degradation properties of the weakly polar acetochlor and strongly polar RhB (see Fig. 1) were also compared and confirmed through extending this BiOBr photocatalytic degradation to other weakly or strongly polar substrates in water.

2. Experimental

2.1. Materials

The acetochlor standard was purchased from Aladdin Reagents Company (Shanghai). A stock aqueous solution of RhB (240 mg/L) was prepared. All of the reagents were of analytical grade and used without further purification. Doubly distilled water was used in all of the experiments.

BiOBr was prepared according to the method previously reported by our group [11]. In this study, two BiOBr catalysts with different specific areas were prepared (i.e., 1#BiOBr BET $\sim 7.2 \text{ m}^2/\text{g}$, 2# BiOBr BET $\sim 10.8 \text{ m}^2/\text{g}$ (determined by N_2 adsorption method). In addition to the specific surface area, no differences in the crystal structure and composition of the catalysts were identified based on XRD analysis. The characterization data of BiOBr used in this research were listed in supporting information (Figs. S1–S3).

2.2. Photocatalysis

A 500 W halogen lamp was used as the visible light source. This lamp was positioned inside the XPA photochemical reaction instrument (Xujiang Electromechanical Plant, Nanjing, China). To ensure

that the system was only irradiated by visible light ($\lambda \geq 420 \text{ nm}$), any light with $\lambda \leq 420 \text{ nm}$ was completely removed by a cutoff filter ($\Phi = 3 \text{ cm}$). In a typical degradation reaction, 30 mL of acetochlor (10.0 mg/L) and 45 mg of BiOBr (1.5 g/L) were added to the Pyrex reaction vessel followed by irradiation of visible light. Generally, the pH of the reaction solutions needed not adjust. At pre-specified reaction times, 1 mL reaction mixture was collected, centrifuged, extracted and analyzed by GC and GC–MS.

2.3. Adsorption experiment

Different dose of BiOBr was added to 30 mL of acetochlor (10.0 mg/L) solution or 30 mL of 7.2 mg/L RhB solution, and the suspensions were magnetically stirred in dark for 24–48 h until adsorption equilibrium was established. Using different catalyst doses, the residual concentrations of acetochlor or RhB were determined, and the adsorption ratios were calculated. RhB was determined using a UV–vis spectrophotometer, and acetochlor was determined by GC.

2.4. Analysis

Dispersive liquid–liquid micro-extraction (DLLME) was used to separate acetochlor from aqueous solution prior to GC analysis [25]. Chlorobenzene (20 μL) was used as the extractant, and acetone (300 μL) was used as the dispersant. For a typical operation, 1 mL sample was transferred to a conical centrifuge tube (2 mL). The extractant was added to the centrifuge tube and shaken vigorously for 30 s, and then centrifuged at 8500 rpm for 10 min, finally 1 μL extractant was withdrawn and injected into the GC for analysis.

Gas chromatography (Varian GC-450) equipped with an electron capture detector (ECD) and a VF-15 ms capillary column (30 m \times 0.25 mm I.D., 0.25 μm film thickness) was used to determine the acetochlor. High purity (99.999%) nitrogen was used as the carrier gas at a constant flow of 1.0 mL/min. The injector was operated in the split mode (50:1) at 260 $^\circ\text{C}$ with a detector temperature of 300 $^\circ\text{C}$. N_2 was used as the make-up gas at a flow rate of 40 mL/min.

The TOC was measured with a N/C 2100 TOC analyzer (Jena, Germany), and the COD was determined according to HJ/T 399–2007.

3. Results and discussion

3.1. Photocatalytic degradation of acetochlor by BiOBr

Fig. 2A shows the gas chromatograms of acetochlor in the samples collected at different reaction times. The retention time of acetochlor was 14.9 min. The peak areas of acetochlor decreased with extending the reaction time from 2 to 10 h, while the peak areas of the degradation products (retention times are 13.8 min, 14.4 min, 15.0 min, 15.7 min, and 16.1 min, respectively) increased.

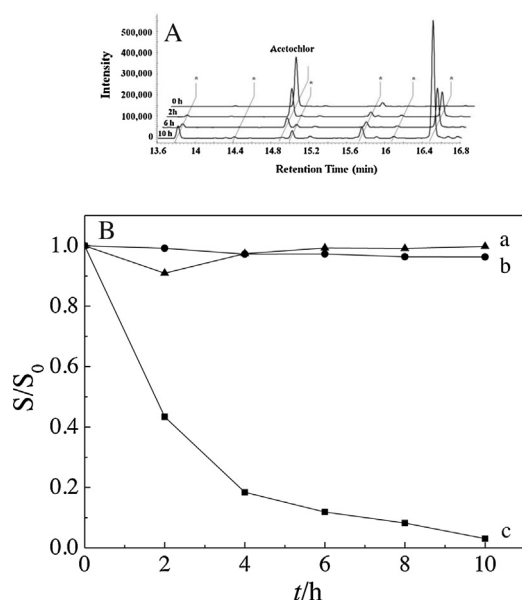


Fig. 2. (A) Gas chromatograms for acetochlor and its degradation products and (B) kinetic curves of acetochlor degradation. (a) dark/BiOBr/acetochlor; (b) vis/acetochlor; (c) vis/BiOBr/acetochlor. Initial reaction conditions: acetochlor, 10 mg/L; BiOBr (1#) 1.5 g/L; pH 5.76.

These results indicated that BiOBr is capable of decomposing weakly polar acetochlor under visible light irradiation.

The kinetic curves for acetochlor photocatalytic degradation were obtained through determination of samples collected at different irradiation time by GC. Fig. 2B shows the acetochlor peak area ratio (S/S_0) as a function of the reaction time. In the control experiments, no degradation of acetochlor was observed in the absence of visible light irradiation (a) or BiOBr (b). However, in the presence of BiOBr and visible light (c), degradation was completed (about 97%) after 10 h. The pseudo-first order reaction rate constant (k) was 0.42 h^{-1} at this point. The BiOBr/vis system at a natural pH effectively degrades weakly polar acetochlor dispersed in water.

The presence of degradation products (Fig. 2A) indicates that acetochlor was not completely mineralized. So, we further examined the COD and TOC changes of acetochlor degradation solutions.

3.2. Changes in COD and TOC during acetochlor degradation

The changes in the COD and TOC during acetochlor degradation are shown in Fig. 3. Under visible light irradiation extending to 40 h, the COD removal and mineralization were 73% and 54%, respectively. Most of the acetochlor was converted to H_2O , CO_2 , Cl^- and other inorganic ions.

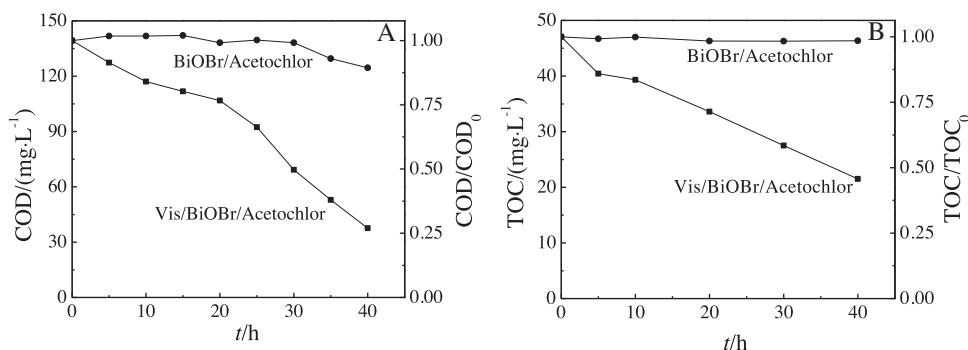


Fig. 3. COD (A) and TOC (B) removal during the degradation of acetochlor. Initial reaction conditions: acetochlor 50 mg/L, BiOBr (1#) 1.5 g/L, pH 5.76.

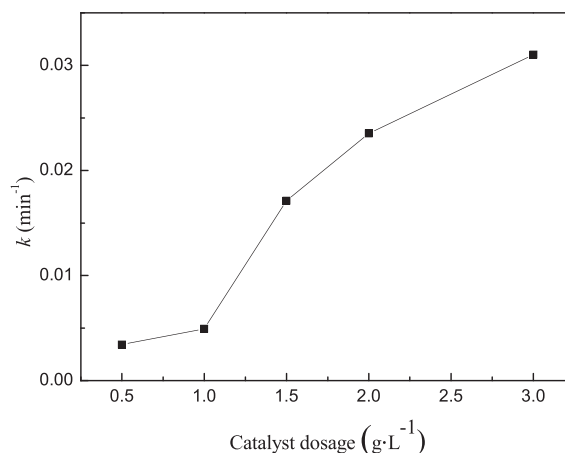


Fig. 4. Effect of pH on the degradation rate of acetochlor. Initial reaction conditions: acetochlor, 10 mg/L; BiOBr (1#) 1.5 g/L.

3.3. Effect of pH on acetochlor degradation

To determine the effect of pH on the degradation of acetochlor, the pH value of the acetochlor solutions was adjusted with HNO_3 or NaOH solution. Fig. 4 shows the degradation extent of acetochlor at different pH values for 3.5 h irradiation. The optimum pH for the degradation was 5.76, which is the natural pH value of the 10 mg/L acetochlor aqueous solution prior to adjustment.

3.4. Dose-rate relationship for the degradation of acetochlor and RhB

Many studies on the degradation of organic pollutants using BiOBr as a photocatalyst under visible light have been reported. However, most of these studies have focused on strongly polar organic compounds containing carboxyl, phenolic hydroxyl, amino group, or sulfonic acid groups (e.g., RhB) [16–18]. These groups are preferentially adsorbed on the surface of BiOBr and readily react with photo-induced holes (h_{vb}^+) or other active oxygen species on the catalyst surface. Because the reaction of the photo-induced electron (e_{cb}^-) in the conduction band is typically limited by the concentration of dissolved dioxygen, the $h_{\text{vb}}^+ - e_{\text{cb}}^-$ recombination process is generally inevitable, and hence, sets the maximum quantum efficiency as a function of the specific surface area of catalyst. Theoretically, at a given photon flux and area of light irradiation for the photoreactor, there is an optimal solid-catalyst dosage in the suspension system. Generally, the maximum light reaction area of a catalyst will not exceed the area of incident light exposure in the reactor. An excessive dose of photocatalyst only increases the adsorption of pollutants but does not enhance their

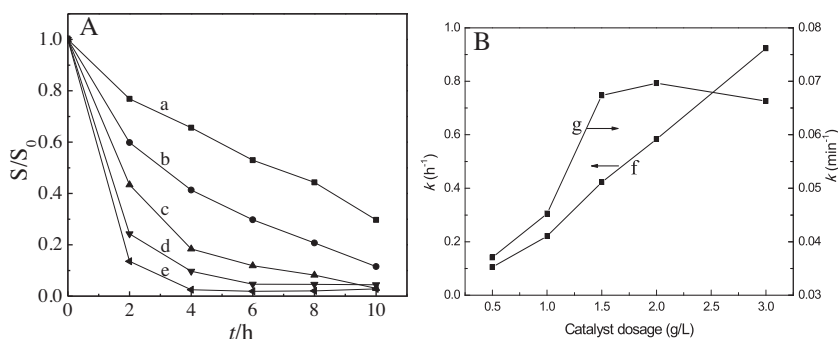


Fig. 5. (A) Effect of the catalyst dose on the degradation of acetochlor: (a) 0.5 g/L, (b) 1.0 g/L, (c) 1.5 g/L, (d) 2.0 g/L, and (e) 3.0 g/L. (B) Comparison of dose-rate relationship: (f) acetochlor and (g) RhB. Initial conditions: acetochlor, 10 mg/L; RhB 7.2 mg/L, pH 5.76. BiOBr photocatalyst was 1#.

photodegradation efficiency because many solid particles in solution prevented from the incident light passing through the reaction solution. Accordingly, photocatalytic reactions of polar compounds, such as RhB, over TiO_2 or other oxide catalysts typically exhibit a degradation efficiency that increases as the catalyst dose increases prior to reaching a platform. Indeed, this effect was also observed for RhB degradation in the BiOBr system (Fig. 5B, curve g). The degradation rate of RhB was not increased by using catalyst dosage higher than 1.5 g/L. This dependences of reaction rate on the catalyst dosage was consistent with the previous observations about photocatalytic degradation of nearly all of polar substrates by metal oxide semiconductor such as TiO_2 and ZnO.

However, that is not what happened for the degradation of weakly polar organic compound acetochlor in water by BiOBr. As shown in Fig. 5A, when the catalyst BiOBr dosage increased, the degradation rate of acetochlor increased exponentially with the dose, and no plateau was observed even at a dose of 3.0 g/L (Fig. 5B, curve f). Therefore, with the same incident light intensity, a satisfactory degradation rate of these weak polar pollutants in water can be achieved by simply adding more catalyst to the reaction system. For example, the half-life ($t_{1/2}$) of 10 mg/L acetochlor is 8 h at a catalyst dosage of 0.5 g/L, which is reduced to 1.5 h at a dose of 3.0 g/L. The light utilization efficiency was increased by a factor of five. To the best of our knowledge, this unique relationship between degradation characteristic to catalyst dosage for weakly polar organic pollutants in water has not been previously reported.

To determine why acetochlor photocatalytic degradation differs from strongly polar RhB degradation, the adsorption behavior of acetochlor and RhB on BiOBr was investigated. Table 1 shows the percentage of remaining acetochlor and RhB in solution at different doses of BiOBr after equilibrium. Surprisingly, acetochlor reached a saturation adsorption at a dose of 1.0 g/L, and the adsorption of RhB increased with the catalyst dosage. The latter behavior is in agreement with previously reported results. However, the adsorption behavior of acetochlor on BiOBr was significantly different from that of strongly polar substrates on traditional solid oxides. In water, the adsorption of acetochlor on the BiOBr surface was influenced by the increase of surrounding BiOBr particles. An increase in the BiOBr dosage causes partial desorption and redistribution of the adsorbed acetochlor, lowering the mass of acetochlor adsorbed per unit area of catalyst. This difference in adsorption behavior can

Table 1
Substrate remaining in solution (%) at various BiOBr (1# SSA 7.2 m²/g) dosages.

Dose of BiOBr	0.5 g/L	1.0 g/L	1.5 g/L	2.0 g/L	3.0 g/L
Acetochlor ^a	72.5%	70.6%	66.2%	66.1%	66.3%
RhB ^b	88.4%	87.8%	86.1%	83.2%	79.5%

^a $C_{\text{acetochlor}} = 10 \text{ mg/L}$.

^b $C_{\text{RhB}} = 7.2 \text{ mg/L}$.

Table 2

Substrate remaining in solution (%) at various BiOBr (2#, SSA 10.8 m²/g) dosages.

Dose of BiOBr	0.5 g/L	1.5 g/L	3.0 g/L	6.0 g/L	9.0 g/L
Acetochlor ^a	86.2%	73.9%	74.4%	\	73.0%
RhB ^b	93.6%	83.5%	73.6%	53.0%	41.9%

100 μL samples add to 3 mL double distilled and then detection.

^a $C_{\text{acetochlor}} = 10 \text{ mg/L}^{-1}$.

^b $C_{\text{RhB}} = 7.2 \text{ mg/L}$.

be correlated with the different dose-rate relationships between acetochlor and RhB.

To further confirm the observed degradation and adsorption characteristics for acetochlor in water mediated by the BiOBr photocatalyst, we prepared another batch BiOBr (2#, 10.8 m²/g SSA) sample with a slightly larger specific surface area than that of BiOBr 1#. Another adsorption experiment and a set of photocatalytic degradation reactions were carried out using a larger range of catalyst dosage. Fig. 6A shows the acetochlor degradation curves with catalyst doses of 0.5 g/L, 1.5 g/L, 3.0 g/L and 9.0 g/L. Similar to BiOBr (1#) case, the degradation rate of acetochlor photocatalyzed by the 2# sample increases with the dosage even up to 9.0 g/L BiOBr dosage. The RhB degradation increased with the BiOBr dosage and reached a maximum rate at 3.0 g/L. Fig. 6B shows that the dose-rate relationship of acetochlor (e) and RhB (f), respectively. As shown in Tables 1 and 2 and Fig. 6B, although BiOBr 1# and BiOBr 2# photocatalyst displayed lots of differences in both the adsorption capacity and the degradation activity (likely because of difference in preparation of different batch BiOBr), both two samples have the same variation trend for the treatment of acetochlor and RhB. The repeating occurrence of unusual dependence of degradation on adsorption property in different batch BiOBr catalysts indicated an unknown but solid rule for BiOBr catalyst catalyzing the degradation of weakly polar acetochlor in water.

3.5. Extending to other polar and low polar substrates

In order to confirm the above conclusion, we selected other representative substrates to conduct the degradation and adsorption experiments on BiOBr photocatalyst. Dye methyl orange (MO), a colorless salicylic acid (SA) (Fig. 7) were chosen as polar substrates to further expand substrate available range (Table S1, Fig. S4) (Table S2, Fig. S5). The results showed that the adsorption and degradation property of MO and SA, respectively, mediated by photocatalyst BiOBr were highly similar to that of RhB case. Simultaneously, other two weakly polar pesticides, propachlor and beta-cypermethrin (Fig. 7), were also used to be degraded in the aqueous solutions by BiOBr under the irradiation of visible light. BiOBr can readily degrade propachlor (Figs. S6 and S7) and beta-cypermethrin (Figs. S8 and S9). More importantly than all of that, with the increase

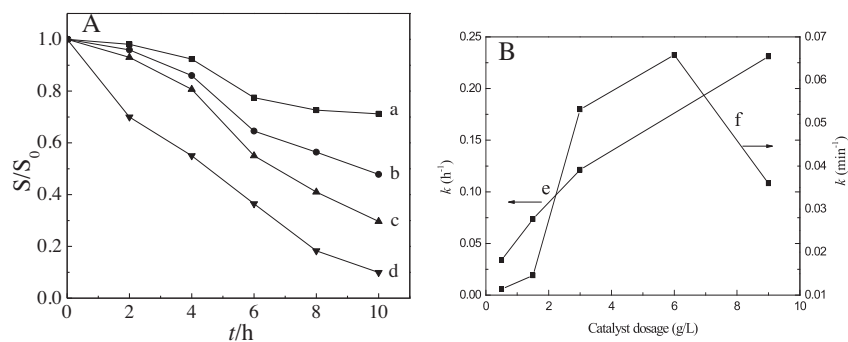


Fig. 6. (A) Effect of catalyst dose on the degradation of acetochlor: (a) 0.5 g/L, (b) 1.5 g/L, (c) 3.0 g/L, and (d) 9.0 g/L. (B) Comparison of dose-rate relationship: (e) acetochlor and (f) RhB. Initial conditions: acetochlor 10 mg/L, RhB 5×10^{-4} mol/L. BiOBr photocatalyst was 2#.

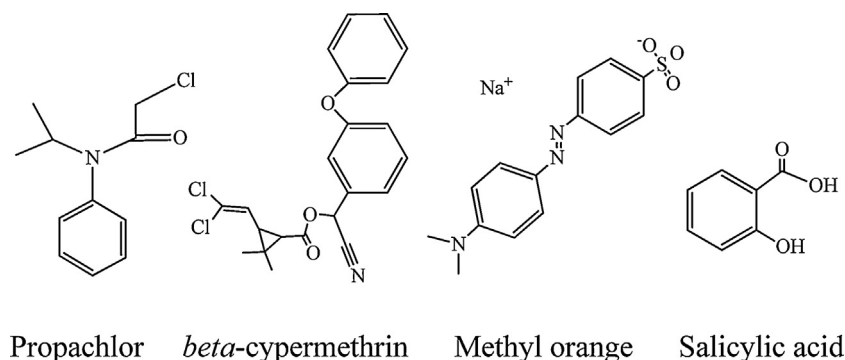


Fig. 7. Structures of propachlor, *beta*-cypermethrin, MO and SA.

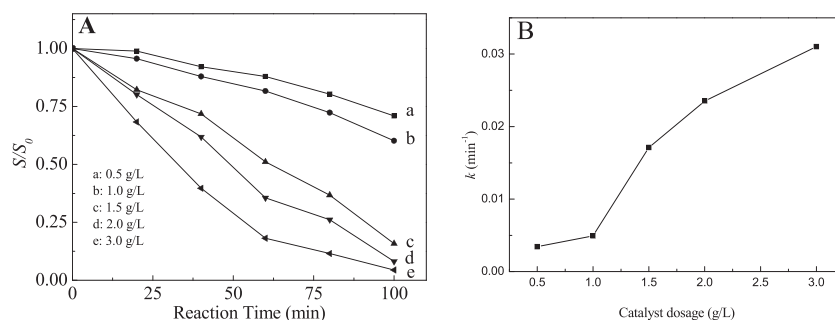


Fig. 8. (A) Effect of the catalyst dose on the degradation of *beta*-cypermethrin. (B) Relationship between catalyst dosage and the degradation rate of *beta*-cypermethrin. $C_{\text{beta-CP}} = 4.5$ mg/L; pH 6.34.

of BiOBr dosage, the degradation rate increased continually (Fig. 8 and Fig. S10), very similar to that of acetochlor degradation. To understand why these weakly polar substrates all exhibited similar photodegradation tendency in the presence of BiOBr aqueous solutions, differ from that of all polar substrates tested under otherwise identical conditions, we carried out *beta*-cypermethrin adsorption experiment in BiOBr aqueous solutions to verify the important re-distribution principle on the H₂O/BiOBr interface that all weakly polar substrates followed. Indeed, the adsorption property of *beta*-cypermethrin on BiOBr aqueous solution with various BiOBr dosages (Table 3) was completely same as in the case of acetochlor. With the increase of BiOBr dosage to largely excessive, the adsorbed amounts of *beta*-cypermethrin on BiOBr did not increase with the increase of BiOBr. At this time, more BiOBr added into the solution no longer adsorb more *beta*-cypermethrin, instead, they only play a role to make the *beta*-cypermethrin molecular re-distribute and lower adsorption quality per BiOBr particle. Next, we will discuss

Table 3

Remaining *beta*-cypermethrin (%) in solution at various BiOBr dosages.

Dosage of BiOBr	0.5 g/L	1.0 g/L	1.5 g/L	2.0 g/L	3.0 g/L
Remaining cypermethrin	54.9%	56.3%	43.8%	44.4%	45.9%

$C_{\text{cypermethrin}} = 4.5$ mg/L⁻¹; stirred in dark for 48 h.

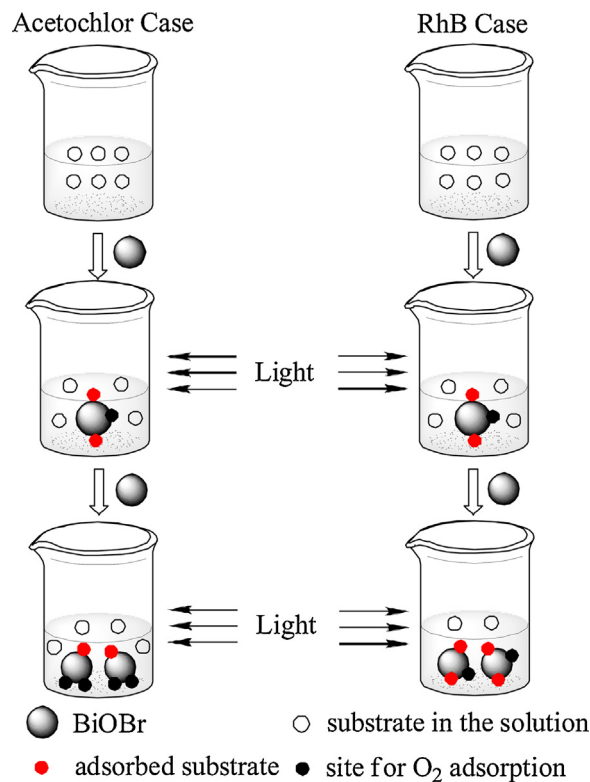
the difference in adsorption properties between polar and weakly polar substrates in detail and correlate it with the photocatalytic mechanism of BiOBr system.

3.6. Discussion of adsorption and degradation ways between polar and weakly polar substrates

The gradual increase in the degradation rate with the catalyst dose for weakly polar substrates such as acetochlor in water is a novel photocatalytic phenomenon. This phenomenon is closely

linked to the adsorption behavior of the substrate on the catalyst. The acetochlor that adsorbed on the BiOBr surface desorbs and re-distributes more easily than polar substrates such as RhB, MO, SA due to their weak polarity, and in fact, its saturation adsorption capacity will significantly change as more BiOBr particles are added. In other words, as the catalyst concentration increases, the saturation adsorption capacity of the unit specific surface area decreases dramatically due to the surrounding suspended polar BiOBr particles. This behavior is the opposite of the conventional trend for the adsorption behavior of oxides in aqueous solutions. For example, in Table 1, at a catalyst dosage of 1.0 g/L, 0.011 mmol of acetochlor were adsorbed per gram of catalyst, and when the dosage of BiOBr increased to 3.0 g/L, the saturated adsorption capacity significantly decreased to 4 mmol/g BiOBr, which is nearly three fold less. The newly added catalyst results in the re-distribution of the substrate that had already reached adsorption equilibrium. The variable adsorption equilibrium may result from the unique distribution characteristics of weakly polar acetochlor on a polar oxide catalyst surface. In contrast, water-soluble RhB quickly adsorbed on BiOBr, and an increased catalyst dose typically did not disrupt the adsorbed RhB. The catalyst adsorbed free RhB more easily in an aqueous solution. Therefore, the adsorption capacity increased with the catalyst dose until a new equilibrium was achieved. Obviously, this strange re-distribution effect seems only to work for weakly polar molecules on the present $\text{H}_2\text{O}/\text{BiOBr}$ interface. Even when the concentration of acetochlor was very low, the adsorption of acetochlor still could not approach to 100% regardless of an excessive usage of catalyst. This is totally different from the conventional adsorption behavior of polar substrates such as RhB on BiOBr, in which normal adsorption capacity will not change with the change of solute concentration under otherwise identical conditions. The adsorption behavior of RhB on BiOBr in aqueous solutions is consistent with the traditional theory and reported results based on other metal oxides, such as TiO_2 and ZnO . Based on our adsorption and degradation results, we proposed a schematic diagram to account for the different photocatalytic degradation rate-catalyst dose relationships for acetochlor and RhB (Scheme 1).

For most photocatalytic degradation reactions, dioxygen is used as the final oxidant to (i) mainly remove e_{cb}^- to sustain h_{vb}^+ continuous generation and (ii) sometimes directly react with the organic free radicals [9]. In general, dissolved dioxygen must be adsorbed on the surface of the catalysts for an effective ET reaction with e_{cb}^- . Therefore, the competing adsorption phenomena always exist between dioxygen and the substrate in a photocatalytic suspension. The dioxygen adsorption and subsequent reaction are important steps in photocatalysis, and these steps are often the rate-determining steps [26–30]. For the current BiOBr photocatalytic system, under otherwise identical conditions, the available adsorption sites increased as the catalyst dose increased for a general polar solute, such as RhB. In contrast, the adsorption sites for acetochlor decreased as the catalyst dose increased. Therefore, this difference will significantly affect the adsorption behavior of dissolved dioxygen and its subsequent reaction. For RhB (Scheme 1), the adsorption sites for dioxygen per catalyst particle did not substantially increase with the addition of more catalyst due to the strong adsorptive ability of RhB. Therefore, the degradation rate does not further increase with an increase in the catalyst dose when the intensity of the visible light irradiation remains unchanged. The saturation of the degradation rate was observed with the increase in the addition of catalyst dosage (Figs. 5 and 6), and this rate decreases with an excessive catalyst dose due to blocking of the light. However, in the weakly polar acetochlor case, the adsorption of acetochlor decreases as the catalyst dose increases. We tentatively imagine that the adsorption action between BiOBr particle and polar acetochlor is weak interaction originated from exposed covalence Br–O within a tetrahedral structure. Such a weak non-



Scheme 1. Two adsorption patterns on photocatalyst BiOBr particles.

polar interaction will be significantly decreased with an increase in the number of surrounding polar catalyst particles (Scheme 1). Therefore, the adsorption of dioxygen and its subsequent reactions will be significantly enhanced with the increase in the catalyst dose unless the lack of light becomes dominant. For any substrate in water, h_{vb}^+ oxidation is a fast and important step due to its strong oxidation potential, and e_{cb}^- removal through the reduction of O_2 is typically a slow and rate-limiting step. Therefore, the effective adsorption and reaction of dioxygen play important roles regardless in the degradation of weakly polar or polar pollutants. The BiOBr photocatalyst provides a new approach based on an increase in the catalyst dose to significantly increase acetochlor degradation. However, further evidence is still required to support this novel mechanism.

4. Conclusions

In this study, the photocatalytic degradation characteristics of acetochlor by BiOBr under visible light irradiation were studied. The relationship between the degradation rate and catalyst dosage of weakly polar acetochlor was compared with that of strongly polar RhB. The results reveal that the two systems exhibited different behaviors, which were closely related to their adsorption behaviors. The saturation adsorption capacity of the weakly polar acetochlor decreased as the BiOBr dose increased in an aqueous solution, which might result from the re-distribution process on BiOBr. This adsorption feature provides more sites for dioxygen to adsorb on BiOBr, in turn provide an efficient way to efficiently eliminate e_{cb}^- to accelerate the degradation rate. In addition, BiOBr photocatalytic degradation of the other weakly polar pesticides, propachlor and beta-cypermethrin, and polar compound, MO and SA were employed to verify the universal of substrates. The insights offered here support the efforts focused on the development of more effective catalysts for the photocatalytic degradation of weakly polar organic compounds in water.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (Nos. 21377067, 21207079, 21177072).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.08.002>.

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